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Synthesis of Mullite Powder and its Characteristics

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SUMMARY

Mullite of stoichiometric composition $3Al_2O_3 \cdot 2SiO_2$ *was synthesised using γ-aluminium oxide and colloidal silicon dioxide. γ-Aluminium oxide was hydrolysed at 90°C and peptised using concentrated nitric acid at 95°C under refluxing conditions for 3 h. The boehmite sol formed was cloudy. Colloidal silicon dioxide was dispersed in acidified water using a mechanical blender and gelled by evaporation of excess water. On calcination of the gel at temperatures above 1300°C for 1 h mullite was formed. The mullite synthesised can be sintered in 3 h at 1650°C to 98·1% of its theoretical density, and shows high flexural strength of 385 MPa (determined in three-point bend) at room temperature.*

1. INTRODUCTION

There are good summary papers by Davis and Pask[1] and Rodrigo and Boch,[2] and a book edited by Sōmiya.[3]

The high temperature strength and creep resistance[4,5] make mullite ($3Al_2O_3 \cdot 2SiO_2$) a suitable material for use in structural ceramic applications. The usual method of synthesising mullite is the thermal treatment of mixed oxides. The product formed contains excess silicon dioxide or aluminium oxide as a second phase.

Mazdiyasni and Brown[6] reported the synthesis of mullite by hydrolytic decomposition of mixed metal alkoxides, which when hot-pressed at 1500°C

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gave a fully dense ceramic with mixed interlocking needle-like, and polygonal, grains. The average flexural strength at room temperature was 128 MPa which increased to 140 MPa at 1400 °C. Ghate *et al.*[7] prepared mullite by using γ-aluminium oxide and amorphous silicon dioxide as base materials. The gel technique was used for mixing and mullite formed only when treated at 1420 °C for 20 h. The particle morphology of the mullite formed was globular. Metcalfe and Sant[8] synthesised mullite by consecutive precipitation of the hydrolysed product of tetramethyl silicate in the presence of aluminium hydroxide. The flexural strength of the sintered body was in the region of 150 MPa. Mullite has also been synthesised under hydrothermal conditions by Roy,[9,10] Sōmiya *et al.*[11] and Suzuki *et al.*[12] In this process, the mixed silicon and aluminium alkoxides or sols were treated under 50 MPa at 300–400 °C for 2 h, and the product formed calcined at 1300 °C for 1 h to yield mullite. Later Yamaguchi *et al.*[13] reported that direct hydrothermal treatment of the powder prepared by hydrolysis of mixed alkoxides at 600 °C under 20 MPa for durations longer than 2 h led to the formation of mullite. Kanzaki *et al.*[14,15] synthesised mullite possessing high flexural strength (360–450 MPa) by spray pyrolysis of mixed aluminium nitrate and ethyl silicate solutions. The flexural strengths of the sintered mullites synthesised using the processes described in Refs 6–8 and 11–13 were less than 200 MPa. The low strength may be the result of the formation of glassy phases and/or secondary phases.

Most of the methods described above are essentially small-scale methods and seem unsuitable for extensive upscaling because of the high cost of the starting materials (e.g. aluminium and silicon alkoxides) and the difficulties encountered when handling large quantities of gelatinous materials and in the removal of the unwanted by-products. In the present investigation a different approach has been used. γ-Aluminium oxide, which was used as the source of aluminium oxide, was first hydrolysed and peptised to give a clear boehmite sol. Mixing this sol with silicon dioxide sol resulted in a homogeneous mullite sol, which on gelation, followed by calcination, resulted in stoichiometric mullite. The sintered mullite appeared to contain no grain boundary glass.

2. EXPERIMENTAL PROCEDURE

2.1. Starting materials

γ-Aluminium oxide (UA-5605, Shōwa Keikinzoku Co. Ltd, Japan) was used as the source of aluminium oxide. Colloidal silicon dioxide (Nipsil E220A, Nihon Silica Kogyo Co. Ltd, Japan) was the source of silicon dioxide. The specific surface areas (BET) of the γ-aluminium oxide and the colloidal silicon dioxide were 68 $m^2 g^{-1}$ and 130 $m^2 g^{-1}$, respectively. The impurities present in γ-aluminium oxide were Na (16 ppm), K (5 ppm) and Si (12 ppm). The chemical composition of the colloidal silicon dioxide used was SiO_2 (95·3 %), Al_2O_3 (0·55 %), Na_2O (0·30 %), Fe_2O_3 (0·09 %), TiO_2 (0·09 %) and CaO (0·05 %); loss on ignition, 3·8 %.

2.2. Preparation of boehmite and silicon dioxide sols

Hydrolysis of γ-aluminium oxide was carried out at temperatures above 90 °C under vigorous agitation to form γ-alumina hydrate (γ-$Al_2O_3 \cdot H_2O$), which was peptised using concentrated nitric acid, maintaining a γ-aluminium oxide to concentrated nitric acid molar ratio of 1:0·06. The temperature of peptisation was 95 °C and it was carried out under refluxing conditions. A cloudy sol was formed in 3 h of peptisation at 95 °C.

Colloidal silicon dioxide was dispersed in distilled water under acidic conditions in a mechanical blender. The dispersion formed was slightly cloudy. No settling of silicon dioxide particles was observed even after standing for 12 h.

2.3. Preparation of mullite gel

The boehmite sol formed by peptisation of γ-aluminium oxide was mixed in a blender with the silicon dioxide sol for 30 min. The mullite sol thus formed was gelled to a solid mass by evaporation of the excess water. The pH of the mullite sol before gelation was 1·8.

2.4. Properties

The surface areas of the powders were determined by the standard BET method (model Accusorb 2100E, Micromeritics, USA) which makes use of the nitrogen adsorption/desorption isotherm. The average particle size and the particle size distribution were determined using a laser particle size analyser (Microtrac R model 799-3, Leeds and Northrup, USA).

The crystalline phases in the calcined product were identified by X-ray diffraction (XRD), using Cu–Kα radiation, at 40 kV, 100 A, and a scanning speed of 10° $2\theta\,min^{-1}$. For the determination of the lattice parameters of mullite, high purity elemental silicon was used as an internal standard. The reflections selected for the determination of the orthorhombic cell constants were (250), (520), (002) and (331). The crystallite size of the mullite was determined using the (331) reflection.

The differential thermal analysis (DTA) curve of the gel was taken at a heating rate of 10 °C min^{-1} up to 1400 °C (model MJ800 DR2, Rigaku Denki Co. Ltd, Japan). The infra-red transmission spectrum of mullite was recorded using a JASCO FT/IR-3 Fourier transform infra-red spectrophotometer.

2.5. Microscopic studies

Transmission electron microscope (TEM) micrographs of the mullite powder were obtained after dispersion in water. The microstructures of the sintered polished specimens were observed by scanning electron microscopy (SEM) after thermal etching at 1450 °C, or acid etching using 10% hydrogen fluoride solution for 1 h.

3. RESULTS AND DISCUSSION

3.1. Formation of mullite

The DTA heating curve of the gelled mullite powder was recorded in ambient atmosphere from 20 °C to 1400 °C at a heating rate of 10 °C min^{-1}, and is shown in Fig. 1. The endotherms at 96 °C and 420 °C represent the loss of moisture from the gel, and dehydration of the boehmite to form the spinel phase (γ-Al_2O_3), respectively. The broad endotherm occurring from 540 °C to 1296 °C is associated with the reaction of the spinel phase with amorphous silicon dioxide to form mullite. The exotherm at 1296 °C is an indication of the complete crystallisation of mullite. Similar results were reported by Hoffman *et al.*[16] for diphasic gels prepared by gelling tetraethoxysilane with boehmite sol.

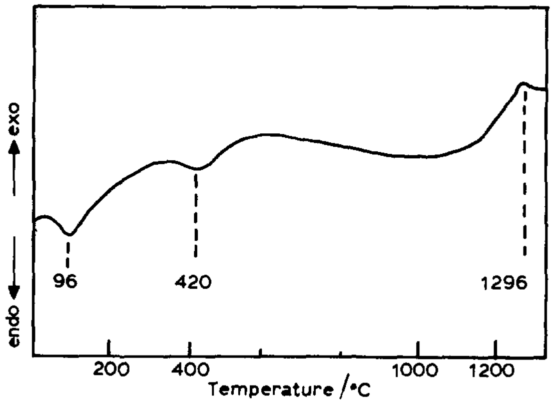

Fig. 1. DTA heating curve of the gelled mullite powder.

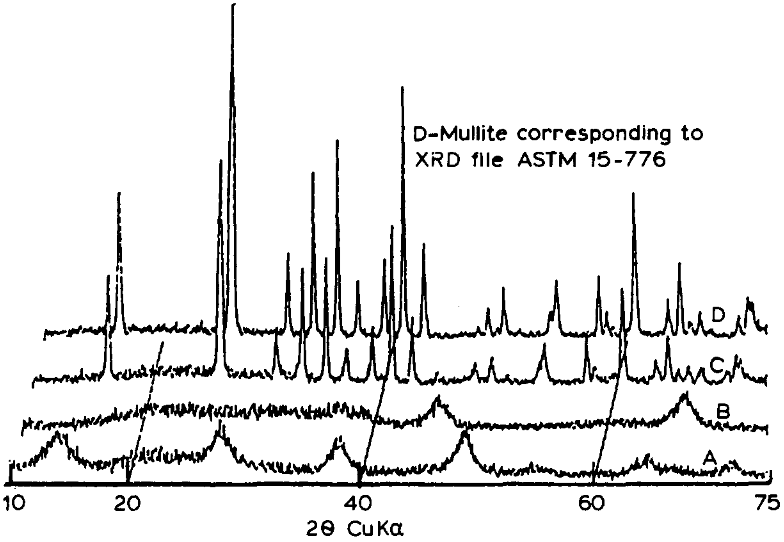

Fig. 2. X-ray diffraction patterns of the gel calcined at different temperatures. A, gel; B, gel at 1000 °C; C, gel at 1300 °C for 1 h; D, gel at 1400 °C for 1 h.

The XRD patterns of the gel mullite, calcined at different temperatures, are shown in Fig. 2. The XRD pattern of the gel shows the presence of boehmite and amorphous silicon dioxide as two discrete phases. These two phases react and at 1000 °C silicon dioxide stabilised δ-aluminium oxide was formed. Amorphous silicon dioxide was also observed. At 1300 °C mullite was observed with traces of δ-aluminium oxide. Similar phenomena were observed by Yoldas[17] in his studies on the Al_2O_3–SiO_2 binary system, and were explained as being due to the stabilisation of active aluminium oxide by silicon dioxide. Only peaks corresponding to mullite were observed when the gel was heated at 1400 °C for 1 h. This phase was retained even after slow cooling and recycling of the same sample several times. This is an indication of the complete solid solution of the mullite.

The chemical composition of the mullite formed is given in Table 1. The lattice parameters of the mullite formed at 1400 °C are $a = 0{\cdot}7566$ nm, $b = 0{\cdot}7684$ nm and $c = 0{\cdot}2887$ nm. The mean crystallite size is 29 nm.

3.2. Infra-red spectra

Infra-red transmission spectra of mullite was observed using potassium bromide discs over the region 1400–400 cm^{-1}. The infra-red transmission spectrum of mullite synthesised at 1400 °C is given in Fig. 3. The observed infra-red-active Al–O tetrahedral vibrations are 1170 cm^{-1}, 865 cm^{-1} and 740 cm^{-1}; Si–O tetrahedral vibrations are 1135 cm^{-1}, 940 cm^{-1} and

TABLE 1
Chemical Composition of the Synthesised Mullite

Constituents	*% by weight*
Al_2O_3	72·0
SiO_2	28·0
Na_2O	0·03
K_2O	0·01
TiO_2	0·13
Fe_2O_3	0·01

505 cm^{-1}; Al–O octahedral vibrations are 580 cm^{-1} and 570 cm^{-1}. The vibrations observed at 1135 cm^{-1}, 740 cm^{-1} and 570 cm^{-1} differ from the frequencies calculated for mullite by MacKenzie.[18] This may be due to the thermal history of the present mullite sample.

3.3. Physical properties of mullite

The surface areas (BET) and calculated average particle sizes of the gel and mullite are given in Table 2. The surface area (BET) of the gel is 277 m^2 g^{-1} which indicates that the gel consists of ultrafine particles of the order of 7 nm

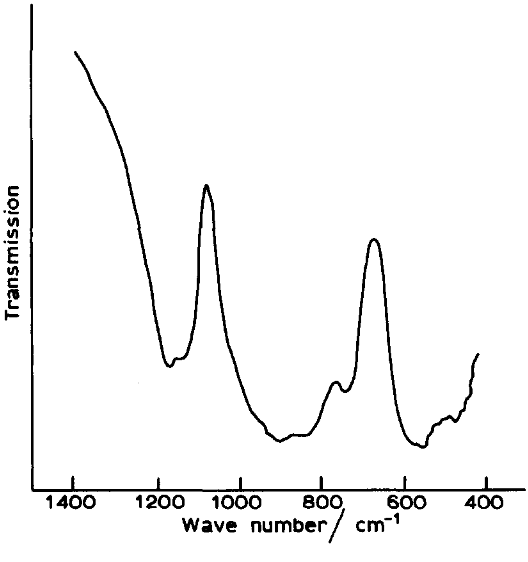

Fig. 3. Infra-red spectrum of mullite recorded using a potassium bromide disc. (Mullite synthesised at 1400 °C for 1 h.)

TABLE 2
BET Surface Area and Particle Size Data

Material	*Surface area/m^2 g^{-1}*	*Average calculated particle size/nm*
Mullite gel	277	7
Mullite (1 400°C calcine)	1·7	1 090
Mullite (milled ultrafine powder)	12·0	160

in dimension. On calcination at 1400°C for 1 h these ultrafine particles undergo sintering, with a decrease in surface area to 1·7 m^2 g^{-1}. The average particle size of the mullite formed at 1400°C for 1 h, as determined by particle size analysis, was 7·5 μm; 90% of the particles were smaller than 26 μm and 10% of the particles were smaller than 1·4 μm. This indicates the presence of particle agglomerates. Milling of mullite was carried out in an attrition mill using zirconia balls. The particle size distribution of the milled mullite is shown in Fig. 4. The average measured particle size of the milled mullite was 1·3 μm, with 90% of the particles smaller than 3·0 μm, and 10% smaller than 0·5 μm. The surface area (BET) was 12 m^2 g^{-1}, and agglomeration is again indicated.

The TEM micrographs of mullite powder synthesised at 1400°C are shown in Fig. 5. The synthesised mullite shows a chunky habit. Von Lohre and Urban[19] found that mullite prepared in the absence of a glassy phase invariably led to a 'chunky' habit, whereas the needle-like morphology formed only in the presence of a liquid phase.

The thermal conductivity of the synthesised mullite was 0·0864 W m^{-1} k^{-1}

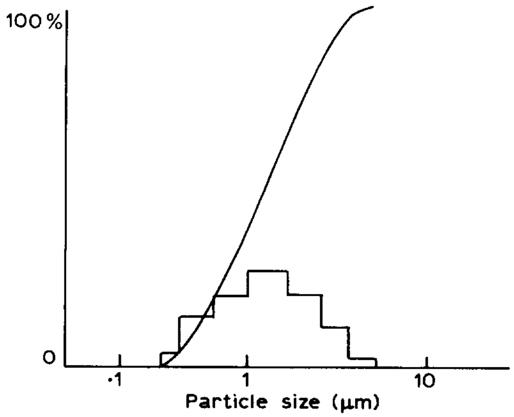

Fig. 4. Particle size distribution of milled calcined mullite powder.

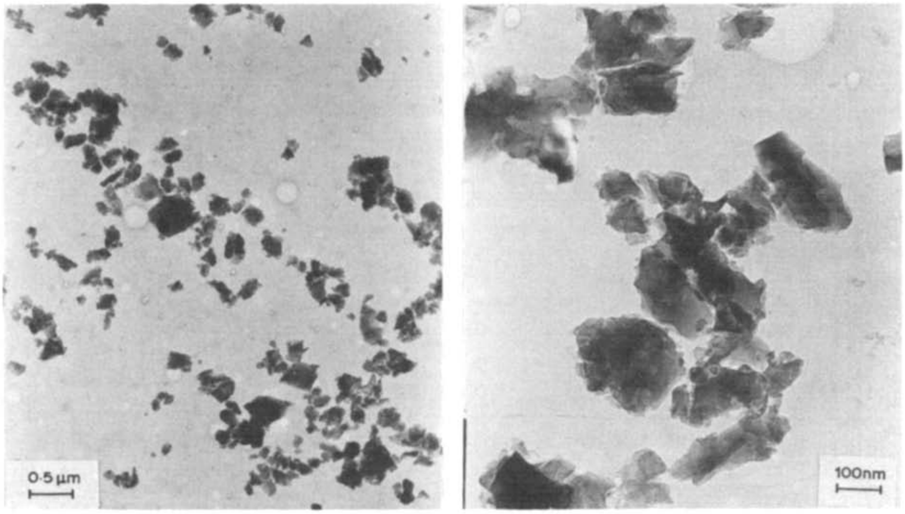

Fig. 5. TEM micrographs of mullite synthesised at 1400 °C for 1 h.

and the coefficient of linear expansion was $5{\cdot}54 \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$ (25–1500 °C).

3.4. Sintering of mullite powder

Mullite powder was cold isostatically pressed at 200 MPa, and sintered at different temperatures. The green density of the pressed powder compact was 51 % of theoretical (assumed as $3{\cdot}19\ \mathrm{Mg\,m^{-3}}$). The powder sintered to 98 % theoretical density after 3 h at 1650 °C. The SEM micrographs of the polished and thermally etched specimens under different magnifications are shown in Fig. 6. The dihedral angles formed by rectangular grains were $>\pi/3$ and indicate the absence of a glassy phase[20] along the grain boundaries. The SEM micrographs of a specimen etched with 10 % hydrogen fluoride are shown in Fig. 7.

The flexural strength of the sintered specimens was determined by the three-point bend method, using test pieces 4 mm × 3 mm × 40 mm in dimension. The mean flexural strength at room temperature was 385 MPa.

4. CONCLUSIONS

Mullite of stoichiometric composition has been synthesised, using a sol–gel route, from γ-aluminium oxide and colloidal silicon dioxide. Formation of mullite from the gel at temperatures as low as 1300 °C indicates that the

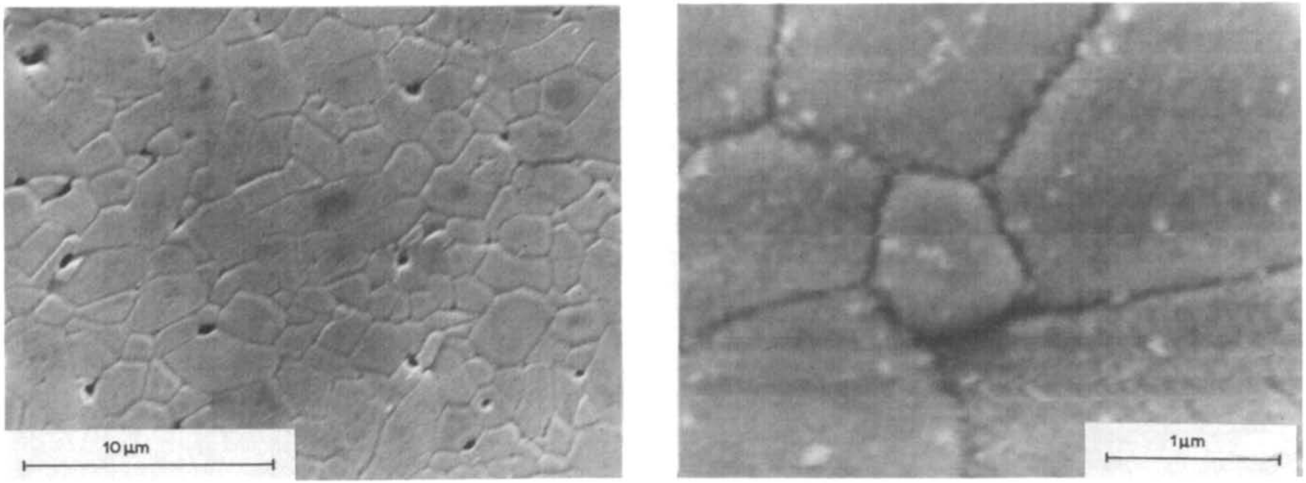

Fig. 6. SEM micrographs of mullite sintered at 1650 °C for 3 h and thermally etched.

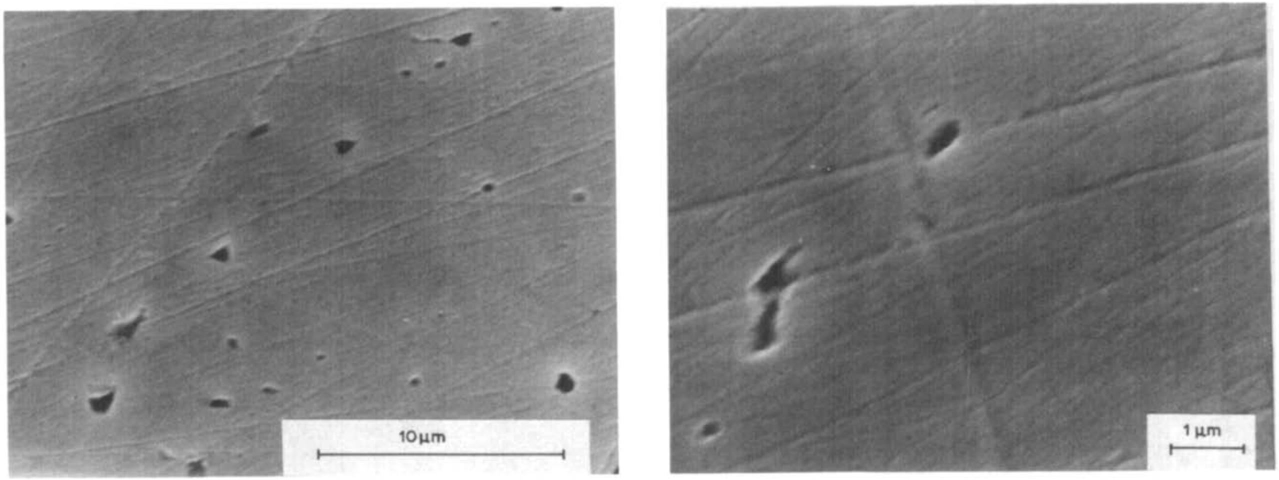

Fig. 7. SEM micrographs of mullite sintered at 1650 °C for 3 h, polished and etched using 10 % hydrogen fluoride for 1 h.

mixing of aluminium oxide and silicon dioxide is homogeneous. In contrast the gel of Ghate *et al.*,[7] formed by mixing γ-aluminium oxide and silicon dioxide, required treatment for 20 h at 1400°C for complete reaction.

The flexural strength at room temperature of mullite formed by sintering at 1650°C for 3 h was 385 MPa. The SEM micrographs of thermally and 10 % hydrogen fluoride etched specimens appeared to show no glassy phase along the grain boundaries, but further experiments are needed to confirm the absence of glass.

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